Incorporation of minor constituents into Portland cement tricalcium silicate

Supporting information

Table SI-1 Detailed Rietveld refinement strategy.

Quantitative phase analysis;
Insertion of more abundant phases and those presenting diffraction peaks without overlapping with other phases (M1 and M3 C3S polymorphs, followed by C3A, Periclase and C4AF respectively) using Fundamental parameters function, concomitantly refining background and scale factors of all phases.
Refinement of unit cell parameters of major phases previously identified, according to weight percentage order, without refinement of the background.
Refinement of crystallite size, limited to the range between 200 and 10000 nm.
Insertion of less abundant phases or those presenting diffraction peaks with high overlapping with other phases (Alpha and Beta C2S polymorphs) using Fundamental parameters function, concomitantly refining background and scale factors of all phases.
Refinement of unit cell parameters of less abundant phases previously identified, according to weight percentage order, without refinement of the background (with exception of the sample HM, in which C2S cell parameters were fixed).
Refinement of the background, unit cell parameters and scale factors of all phases at the same time (with exception of the sample HM, where C2S cell parameters were fixed).
Refinement of peak shape of each phase using pseudo-Voight function.

Refinement of occupancy factors of Fe and Al of C4AF phase.

Revision of M1 polymorph structural model;

Creation of Ca_6O rigid bodies and refinement of their position and orientation, fixing background, scale factors and Ca-O distance.

Refinement of Ca_6O rigid bodies position, orientation and Ca-O bonds lengths, fixing background and scale factors.

Creation of SiO_4 rigid bodies and refinement of their position and orientation, fixing background, scale factors, Si-O distance and Ca-O rigid bodies.

Refinement of SiO_4 rigid bodies position, orientation and Si-O bonds lengths, fixing background and scale factors.

Refinement of Ca_6O and SiO_4 rigid bodies position, orientation and bond lengths.

Refinement of background and scale factors, fixing all atomic positions.

Refinement of Ca, Si and O atomic displacement parameters, fixing background, scale factors and atomic positions.

Table SI-2 Refined atomic positions, occupancy factors and atomic displacement parameters, constrained dependent upon atom type, of the revised M1 model in space group Pc.

Site	X	y	Z	Occ.	B
Ca1	0.08967	0.26107	0.51868	1	0.092
Ca2	0.87395	0.03661	0.68394	1	0.092
Ca3	0.09949	0.47418	0.77084	1	0.092
Ca4	0.21212	0.0065	0.72488	1	0.092
Ca5	0.33044	0.5156	0.99017	1	0.092

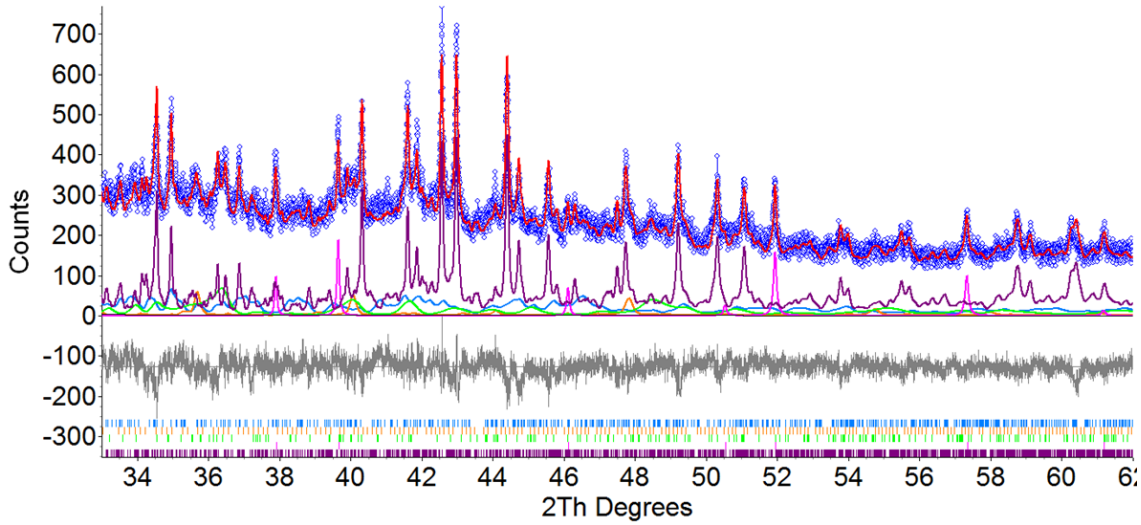
Ca6	0.64626	0.48471	0.45668	1	0.092
Ca7	0.42808	0.47545	0.76207	1	0.092
Ca8	0.65361	0.25224	0.70751	1	0.092
Ca9	0.77519	0.00459	0.75566	1	0.092
Ca10	0.88069	0.24756	0.95438	1	0.092
Ca11	0.99329	0.50448	0.49281	1	0.092
Ca12	0.10443	0.00464	0.74947	1	0.092
Ca13	0.21218	0.26378	0.94083	1	0.092
Ca14	0.32586	0.27408	0.72482	1	0.092
Ca15	0.41886	0.25026	0.5126	1	0.092
Ca16	0.53239	0.48042	0.70556	1	0.092
Ca17	0.65624	0.98629	0.47794	1	0.092
Ca18	0.76189	0.26778	0.51065	1	0.092
Ca19	0.98802	0.03497	0.46132	1	0.092
Ca20	0.75567	0.49939	0.74832	1	0.092
Ca21	0.87969	0.49322	0.71771	1	0.092
Ca22	0.9913	0.24626	0.70822	1	0.092
Ca23	0.20551	0.49973	0.68155	1	0.092
Ca24	0.3193	0.012	0.97753	1	0.092
Ca25	0.55133	0.27752	0.94977	1	0.092
Ca26	0.53656	0.02377	0.69254	1	0.092
Ca27	0.43064	0.00367	0.73698	1	0.092
O1	0.04469	0.26401	0.61081	1	0.535
O2	0.95506	0.23598	0.86582	1	0.535
O3	0.82639	0.26953	0.7492	1	0.535
O4	0.16188	0.24494	0.7457	1	0.535
O5	0.37204	0.25976	0.61499	1	0.535
O6	0.27139	0.27957	0.83161	1	0.535
O7	0.60935	0.27744	0.81185	1	0.535
O8	0.70813	0.25554	0.60893	1	0.535
O9	0.48262	0.26687	0.73443	1	0.535
Si1	0.99162	0.23437	0.22563	1	0.046
O10	0.96913	0.06916	0.14131	1	0.535
O11	0.98804	0.40923	0.15283	1	0.535
O12	0.96027	0.2628	0.29753	1	0.535
O13	0.04906	0.19633	0.31078	1	0.535
Si2	0.20522	0.24467	0.45402	1	0.046
O14	0.1405	0.2443	0.36704	1	0.535
O15	0.23148	0.43889	0.42981	1	0.535
O16	0.2165	0.23567	0.59734	1	0.535
O17	0.23242	0.05989	0.42181	1	0.535
Si3	0.09238	0.25126	0.00892	1	0.046
O18	0.09449	0.43838	0.06887	1	0.535
O19	0.07447	0.28081	0.87525	1	0.535
O20	0.05364	0.12307	0.02755	1	0.535
O21	0.14693	0.16288	0.06402	1	0.535

Si4	0.31546	0.26002	0.22612	1	0.046
O22	0.25181	0.24862	0.16337	1	0.535
O23	0.33909	0.07925	0.1885	1	0.535
O24	0.33707	0.26492	0.37024	1	0.535
O25	0.33389	0.44735	0.18242	1	0.535
Si5	0.53475	0.25077	0.44369	1	0.046
O26	0.46566	0.25543	0.36751	1	0.535
O27	0.55788	0.0364	0.41736	1	0.535
O28	0.55466	0.27804	0.59811	1	0.535
O29	0.56078	0.43331	0.39186	1	0.535
Si6	0.43101	0.23954	0.00409	1	0.046
O30	0.36935	0.23686	0.95535	1	0.535
O31	0.4457	0.22873	0.89582	1	0.535
O32	0.4554	0.06742	0.08928	1	0.535
O33	0.45361	0.42529	0.07591	1	0.535
Si7	0.64672	0.22397	0.22905	1	0.046
O34	0.58798	0.25126	0.1511	1	0.535
O35	0.67715	0.38335	0.20751	1	0.535
O36	0.66414	0.03956	0.19713	1	0.535
O37	0.65761	0.22174	0.3605	1	0.535
Si8	0.87607	0.25494	0.45665	1	0.046
O38	0.80719	0.27613	0.38267	1	0.535
O39	0.90513	0.45227	0.42662	1	0.535
O40	0.89636	0.23709	0.61174	1	0.535
O41	0.8956	0.05433	0.40553	1	0.535
Si9	0.77701	0.23885	0.01811	1	0.046
O42	0.73406	0.35029	0.03166	1	0.535
O43	0.76233	0.21202	0.88556	1	0.535
O44	0.78266	0.04924	0.07778	1	0.535
O45	0.82901	0.34397	0.07744	1	0.535

Table SI-3 Coordinates and occupancy factors of the tetrahedral interstitial sites.

Site	Element	x	Y	z	Occ. factor
Interstitial 1	S^{6+}	0.260340	0.252345	0.340070	0.162
Interstitial 2	Fe^{3+}	0.591062	0.235677	0.330205	0.782

a)



b)

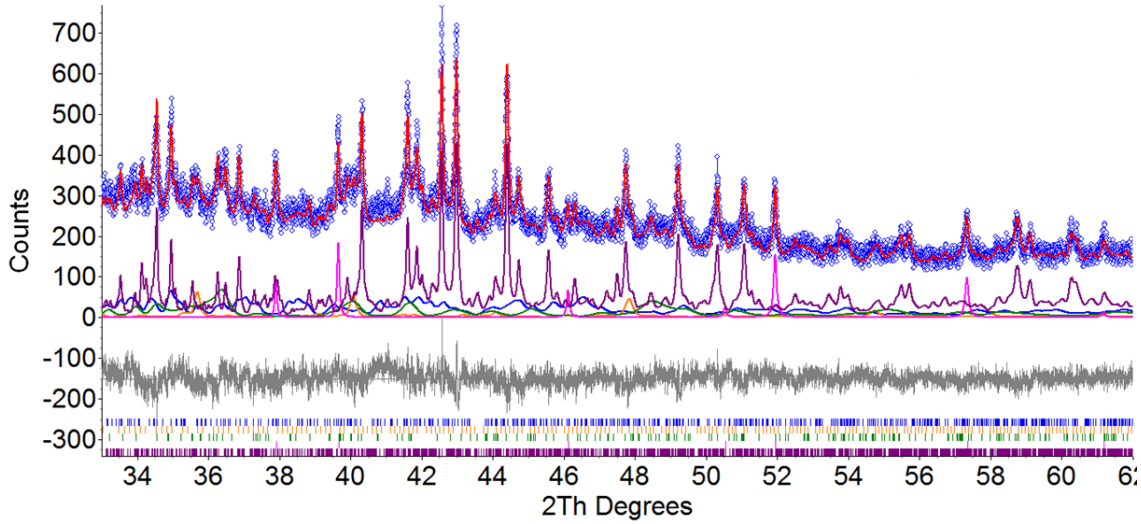
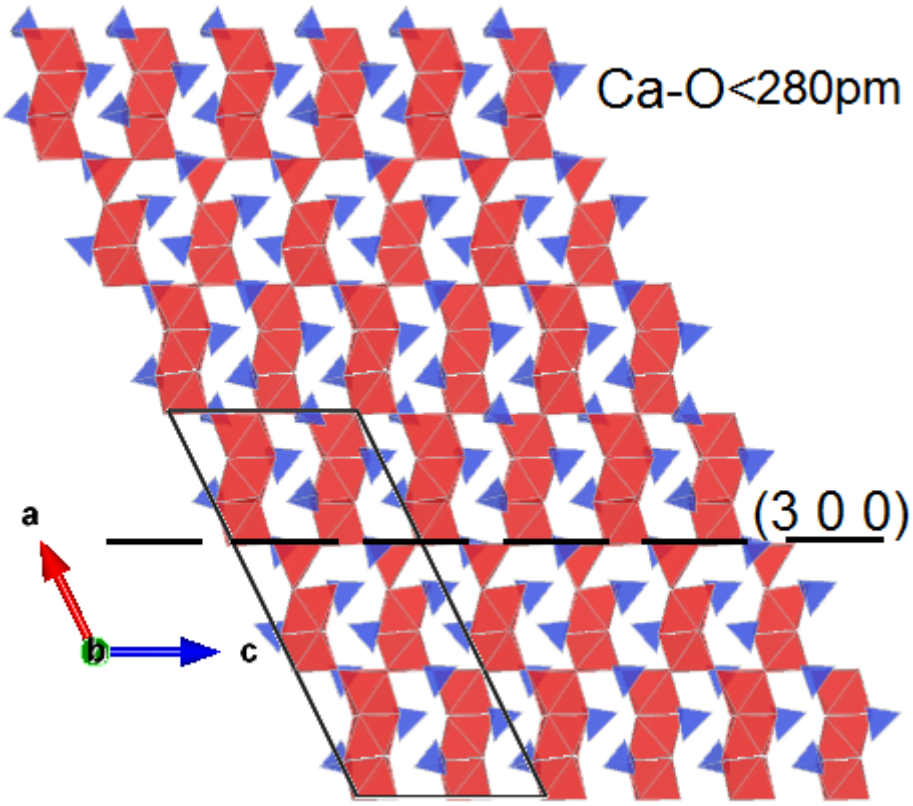
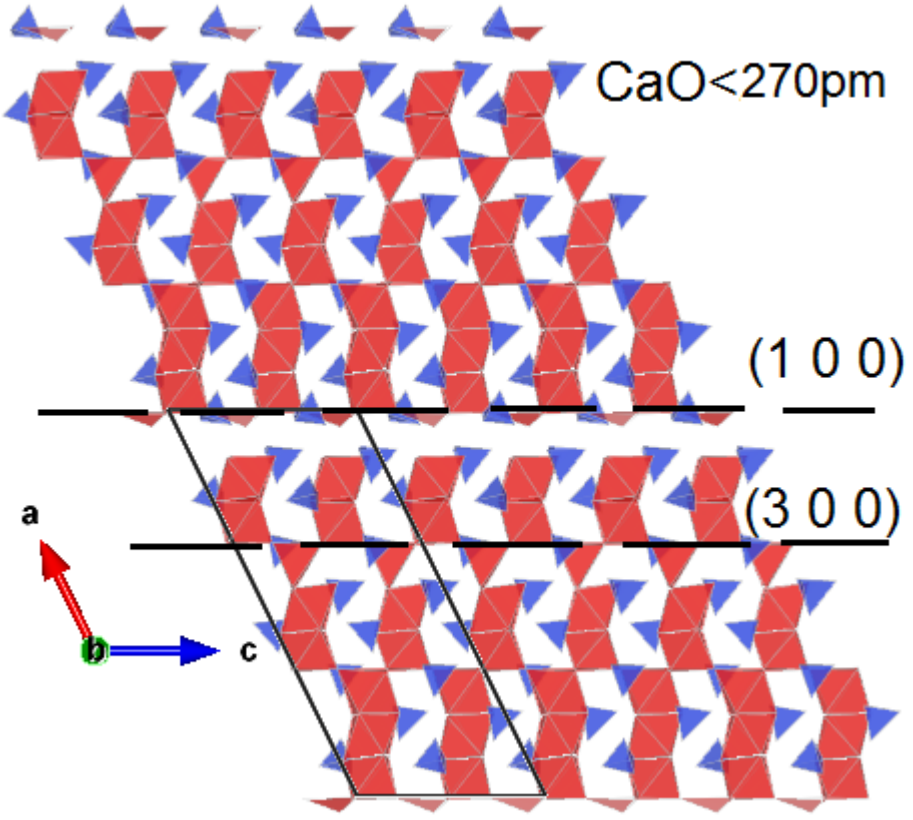


Figure SI-1 High angle range (34 to 62 2θ°) of the observed (blue dot), calculated (red) and difference (grey) profiles from Rietveld refinement of synchrotron PXRD data of HM sample before (a) and after determination of revised atomic parameters for Noirfontaine's M1 Model through refinement of rigid-bodies (b), showing calculated phase profiles of alite M1 (purple), belite (light blue), aluminate (orange), ferrite (green) and periclase (magenta).



a)



b)

Figure SI-2 Crystallographic structural diagrams of the new revised M1 structural model adopting maximum Ca-O bond length < 280 pm (a) and < 270 pm (b), showing the *ac* plane. Dashed/dotted lines represent the (1 0 0) and (3 0 0) planes.

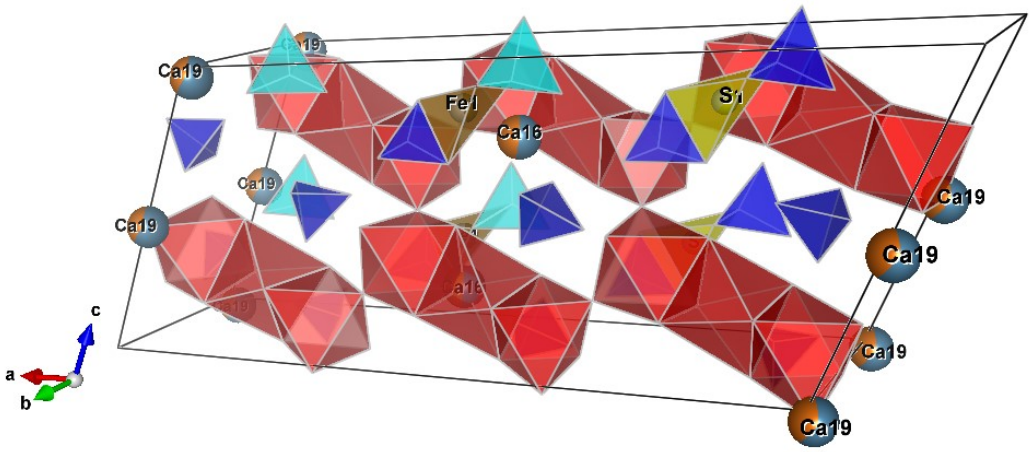


Figure SI-3 Crystallographic structural diagram of the revised M1 structural model showing preferential substitutional sites for Mg^{2+} (partly orange) on Ca^{2+} sites (partly blue) and Al^{3+} (light blue tetrahedra) on Si^{4+} sites (dark blue tetrahedra), as well as interstitial sites S^{+6} (light yellow tetrahedra) and Fe^{3+} (dark yellow tetrahedra).

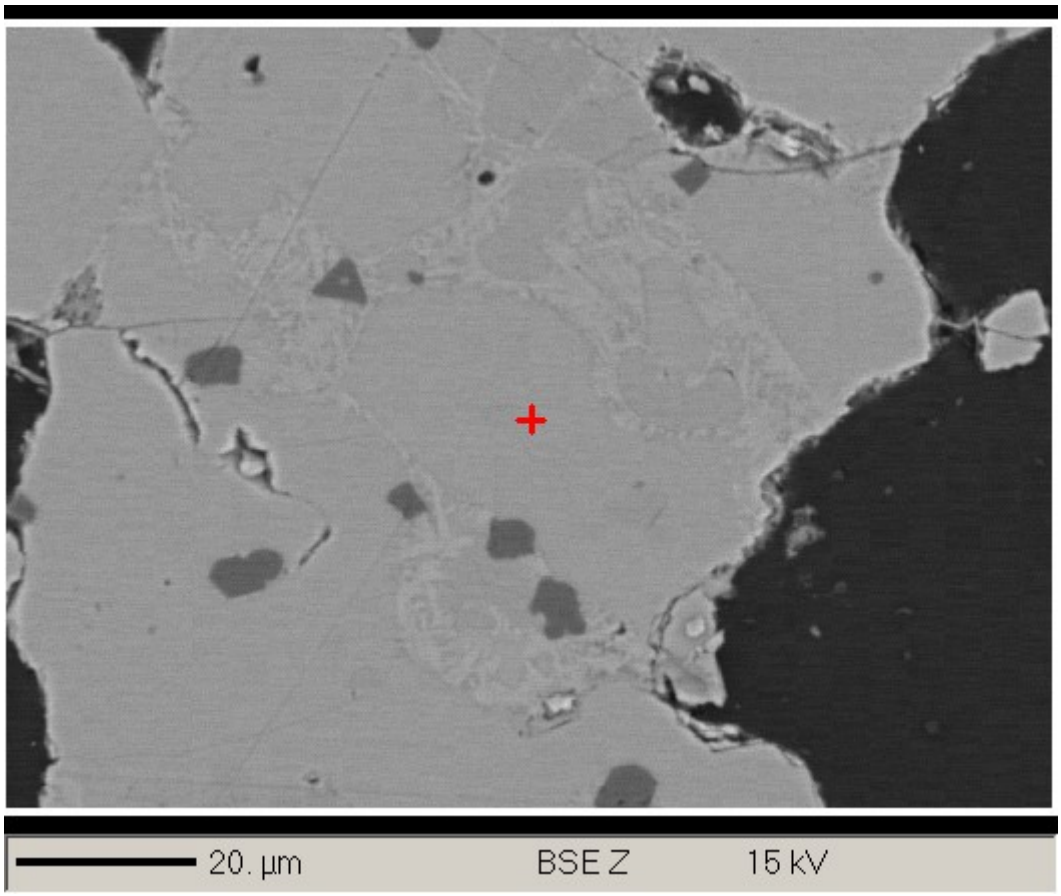
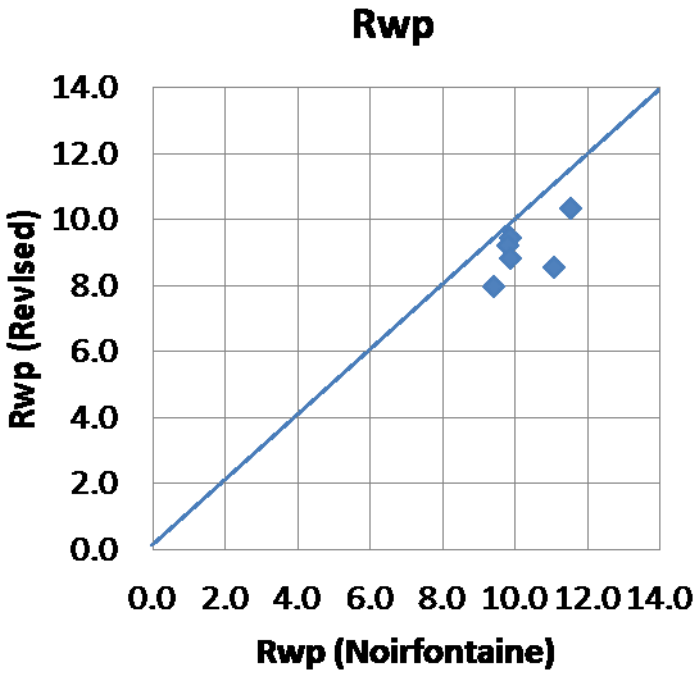
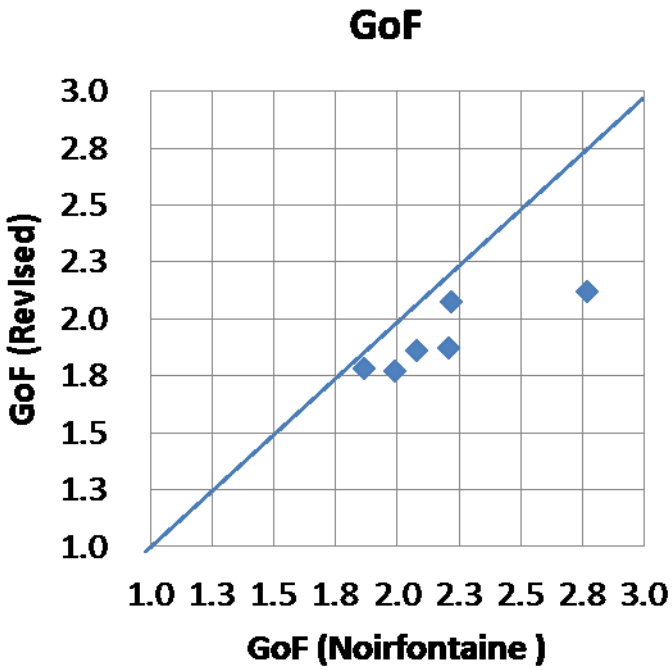


Figure SI-4 Backscattered electron image of point 1 of EPMA analysis of HM clinker sample.



a)



b)

Figure SI-5 Comparison of Rietveld refinement fit indexes (Rwp and GoF) of synchrotron PXRD data of 6 industrial clinker samples using revised C3S M1 model (a) and Noirfontaine's M1 Model (b).